Three-Dimensional Molecular Imaging Secondary Ion Mass Spectrometry

In recent years, the use of cluster primary ion projectiles for organic secondary ion mass spectrometry (SIMS) has generated considerable interest as a method to improve molecular secondary ion yields, facilitate improved sensitivity for large molecule analysis and minimize the accumulation of beam-induced damage in selected organic materials. In this work, we report on our first attempts to combine SF_5^+ primary ion bombardment with secondary ion imaging on an ion microscope SIMS instrument to produce spatially resolved molecular information as a function of depth. Three dimensional (3D) molecular imaging SIMS is achieved by acquiring a series of characteristic molecular secondary ion images as a function of increasing depth during dynamic SIMS sputtering of thin molecular films using cluster primary ion bombardment. Reconstruction of the resulting image stack provides a 3D volumetric image of the molecular composition of the sample. This approach has been used to examine several different types of samples including thin polymer films, multilayer polymer films and polymer films doped with pharmaceuticals.

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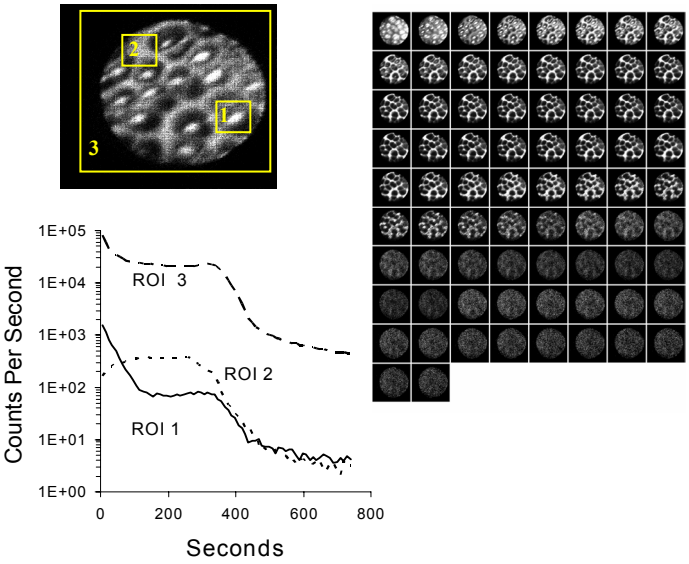
Three-dimensional secondary ion mass spectrometry (SIMS) images have been obtained on the NIST ion microscope SIMS instrument using an SF_5^+ primary ion beam. Microscope imaging eliminates the need for a highly focused ion beam, thus allowing large diameter, higher current, and lower impact energy cluster ion beams to be used which in turn allows for higher sputtering rates, faster analysis times, and increased depth resolution. Also, image acquisition rates can be further increased since the secondary ion signal from each pixel in the image is acquired and digitized in parallel. An example of microscope-based molecular image depth profiling is shown in the figure for a polylactic acid (PLA) film spun cast on silicon. This biodegradable polymer, commonly used in drug delivery applications, was doped with 20% by mass acetaminophen. No degradation in molecular ion signal is observed during the analysis. In this example, the drug is nonuniformly distributed as a function of depth as a result of phase segregation during preparation.

Microscope imaging is particularly well suited for use with cluster ion beam sources because the requirement for a highly focused primary ion beam is eliminated.

This new capability will enable 3D molecular characterization of polymer thin films, pharmaceuticals, drug delivery systems, and biological tissues providing information about the distribution of compounds that has not previously been possible to obtain.



Above is a series of 74 secondary ion images of m/z 152 from acetaminophen-doped PLA polymer film using a 250 µm field-of-view and 10 second image acquisition. Images in this figure are displayed from left to right as a function of increasing depth beginning in the upper left hand corner. Selected area profiles of m/z 152 from the image stack showing variability in drug distribution from different areas of the film are also shown. Volumetric view of the distribution of m/z 152 using all images in the stack.

Future Plans: SF_5^+ molecular image depth profiling has been demonstrated for a series of polymer films, polymer bilayers, patterned polymer films, and polymers containing organic molecules. While this approach is not applicable to all organic materials, it is promising for those materials that are amenable to high primary ion dose analysis by cluster SIMS. This capability is currently being enhanced by the addition of a C_{60} cluster ion source for molecular depth profiling of biological tissue samples.